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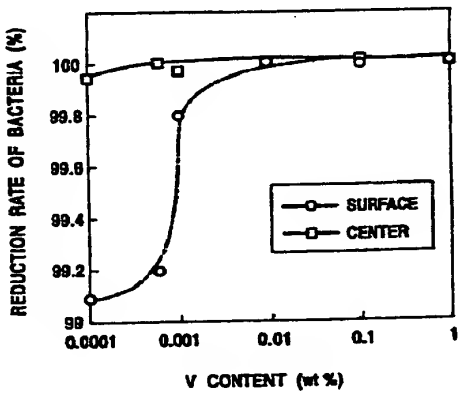
(54) STAINLESS STEEL PRODUCT HAVING EXCELLENT ANTIMICROBIAL ACTIVITY AND METHOD FOR PRODUCTION THEREOF

(57) The present invention provides a stainless steel having superior corrosion resistance, antibacterial properties, and durability, the antibacterial properties being maintained after surface treatments commonly performed including, for example, polishing. In particular, the stainless steel contains not less than 10 percent by weight of chromium, 0.001 to 0.30 percent by weight of silver, or further contains 0.001 to 1.0 percent by weight of vanadium. In addition, not less than 0.0005 weight percent of a silver oxide, the amount thereof being not more than 1.1 times that of the silver, is dispersed in the stainless steel. In order to homogeneously disperse the silver oxide in the stainless steel, when continuous casting of molten steel is performed, the casting rate for the continuous casting is preferably 0.8 to 1.6 m/min. A method for manufacturing the stainless steel is also disclosed.

FIGURE 1



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inventors of the present invention found that the steel provided with the optimum amount of silver homogeneously dispersed therein had stable antibacterial properties for applications in which the steel was subject to mold pressing and polishing, and in which the surfaces of the steel were scrubbed or abraded during use.

[0010] The present invention was accomplished based on the above knowledge in conjunction with further research therefor.

[0011] Accordingly, a first aspect of the invention is that a stainless steel, having antibacterial properties, comprises not less than 10 percent by weight of chromium, 0.001 to 0.30 percent by weight of silver, and not less than 0.0005 percent by weight of a silver oxide, the amount of the silver oxide being not more than 1.1 times that of the silver.

[0012] A second aspect of the invention is that the stainless steel, having the antibacterial properties according to the first aspect of the invention, further comprises 0.001 to 1.0 percent by weight of vanadium.

[0013] A third aspect of the invention is that the stainless steel, having the antibacterial properties according to the first aspect and the second aspect of the invention, further comprises not more than 0.015 percent by weight of sulfur.

[0014] A fourth aspect of the invention is the stainless steel, having the antibacterial properties according to the first aspect to the third aspect of the invention, wherein the silver content is not less than 0.001 and is less than 0.05 percent by weight of the stainless steel.

[0015] A fifth aspect of the invention is the stainless steel, having the antibacterial properties according to the second aspect of the invention, wherein the vanadium content is 0.001 to 0.30 percent by weight of the stainless steel.

[0016] A sixth aspect of the invention is the stainless steel having the antibacterial properties according to the first aspect to the fifth aspect of the invention, wherein the stainless steel is in the form of any one of a sheet, a strip, a pipe, and a wire.

[0017] A seventh aspect of the invention is a method for manufacturing a stainless steel raw material, comprising the steps of controlling amounts of not less than 10 percent by weight of chromium, 0.001 to 0.30 percent by weight of silver, and not more than 0.015 percent by weight of sulfur in molten stainless steel, and performing continuous casting of the molten stainless steel at a casting rate of 0.8 to 1.6 m/min.

[0018] A eighth aspect of the invention is the method for manufacturing the stainless steel according to the seventh aspect of the invention, in which the molten stainless steel further comprises 0.001 to 1.0 percent by weight of vanadium.

[0019] A ninth aspect of the invention is that the method for manufacturing the stainless steel, having antibacterial properties according to the seventh aspect and the eighth aspect of the invention, further comprises the steps of hot rolling and cold rolling.

[0020] The reasons for specifying the chemical composition of the steel according to the present invention will be described hereunder.

[0021] The composition of the stainless steel of the present invention is suitable for the austenitic stainless steel, the ferritic stainless steel, the martensitic stainless steel, and other various stainless steel.

[0022] The chemical composition of the austenitic stainless steel is preferably as follows; 0.001 to 0.1 percent by weight of carbon, not more than 2.0 percent by weight of silicon, not more than 2.0 percent by weight of manganese, not more than 0.1 percent by weight of phosphorus, 10 to 35 percent by weight of chromium, 6 to 15 percent by weight of nickel, 0.001 to 0.1 percent by weight of nitrogen, and the balance being iron and incidental impurities. In addition, one or more elements selected from the group of molybdenum, not more than 3.0 percent by weight; copper, not more than 1.0 percent by weight; tungsten, not more than 0.30 percent by weight; aluminum, not more than 0.3 percent by weight; titanium, not more than 1.0 percent by weight; niobium, not more than 1.0 percent by weight; zirconium, not more than 1.0 percent by weight; cobalt, 0.001 to 0.5 percent by weight; and boron, not more than 0.01 percent by weight, may be included in the austenitic stainless steel.

[0023] The chemical composition of the ferritic stainless steel is preferably as follows; 0.0001 to 0.1 percent by weight of carbon, not more than 1.0 percent by weight of silicon, not more than 2.0 percent by weight of manganese, not more than 0.1 percent by weight of phosphorus, 10 to 50 percent by weight of chromium, not more than 0.10 percent by weight of nitrogen, and the balance being iron and incidental impurities. In addition, one or more elements selected from the group of aluminum, not more than 0.3 percent by weight; nickel, not more than 1.0 percent by weight; molybdenum, not more than 3.0 percent by weight; titanium, not more than 1.0 percent by weight; niobium, not more than 1.0 percent by weight; zirconium, not more than 1.0 percent by weight; copper, not more than 1.0 percent by weight; tungsten, not more than 0.30 percent by weight; cobalt, 0.001 to 0.5 percent by weight; and boron, not more than 0.01 percent by weight, may be included in the ferritic stainless steel.

[0024] The chemical composition of the martensitic stainless steel is preferably as follows; 0.001 to 1.0 percent by weight of carbon, not more than 1.0 percent by weight of silicon, not more than 2.0 percent by weight of manganese, not more than 0.1 percent by weight of phosphorus, 10 to 19 percent by weight of chromium, 0.001 to 0.1 percent by weight of nitrogen, and the balance being iron and incidental impurities. In addition, one or more elements selected from the group of aluminum, not more than 1.5 percent by weight; titanium, not more than 1.0 percent by weight; niobium, not more than 1.0 percent by weight; tungsten, not more than 0.3 percent by weight; zirconium, not more than 1.0 per-

through the steps of hot rolling, annealing for a hot-rolled plate (850°C × 60 seconds), cold-rolling, and bright annealing (850°C × 60 seconds). Stable antibacterial properties were obtained at the center of the steel product regardless of the addition of the vanadium; however, in contrast, at the surface, the antibacterial properties were degraded when the added amount of vanadium was less than 0.001 percent by weight. The reason for this is believed to be that vanadium acts as a so-called " dispersing agent" which remarkably suppress the tendency of silver particles, a silver oxide, and a silver sulfide to be locally concentrated at the central interior of the plate. When the vanadium is contained at not less than 0.001 percent by weight, consistent antibacterial effects at the surfaces of the steel can be obtained. In contrast, when the vanadium content is more than 0.30 percent by weight, the effect described above is saturated, and when the vanadium content is more than 1.0 percent by weight, workability and corrosion resistance tend to be degraded. Therefore, the vanadium in the range of 0.001 to 1.0 percent by weight is preferable. More preferably, the range is 0.001 to 0.30 percent by weight, and further preferably the range is 0.01 to 0.25 percent by weight.

[0034] The stainless steel according to the present invention is composed of the chemical compositions in the ranges described above, and iron and incidental impurities as the balance.

[0035] Since the steel according to the present invention can be manufactured by any one of known steel making techniques, manufacturing methods are not required to be specified. A preferably manufacturing method is, for example, a secondary refining by SS-VOD (Strongly Stirred Vacuum Oxygen Decarbonization) following the step of the steel making technique by using a steel converter, an electric furnace, and the like.

[0036] According to the present invention, a molten stainless steel is manufactured by a known steel making technique, in which the molten stainless steel having a stainless steel composition, provided with not less than 10 percent by weight of chromium, further contains 0.001 to 0.30 percent by weight of silver, or still further contains 0.001 to 1.0 percent by weight of vanadium. The molten steel thus manufactured can be made in steel raw material by using known casting methods; however, in view of productivity and quality, continuous casting is preferably employed.

[0037] In the continuous casting, in order to finely and homogeneously disperse not less than 0.0005 percent by weight of silver oxide in the steel, the casting rate is determined to be in the range of 0.8 to 1.6 m/min. Concomitant with determining the casting rate, the sulfur content in molten stainless steel is determined to be not more than 0.015 percent by weight, and more preferably, not more than 0.010 percent by weight.

[0038] When the casting rate is less than 0.8 m/min, the silver oxide particles become coarse and large, corrosion resistance is degraded, and stable antibacterial properties are thereby difficult to obtain. In contrast, when the casting rate exceeds 1.6 m/min, stable casting is difficult to perform and not less than 0.0005 percent by weight of the silver oxide is not homogeneously dispersed in the steel. Hence, the silver oxide dispersed heterogeneously at the surface of the steel, and stable antibacterial properties during use cannot be obtained. Accordingly, the casting rate in the continuous casting is preferably in the range of 0.8 to 1.6 m/min.

[0039] In order that the silver oxide is in the predetermined range of not less than 0.0005 percent by weight and not more than 1.1 times the amount of the silver (percent by weight) in the stainless steel, the sulfur content in the molten stainless steel is not more than 0.015 percent by weight, more preferably not more than 0.010 percent by weight, concomitant with the casting rate being 0.8 to 1.6 m/min. An adjustment of the sulfur content in the molten stainless steel may be performed by known refining methods and is not particularly specified; however, a desulfurization method by adding a ferrosilicon and calcium compounds in steel converters and/or VOD furnaces is preferable.

[0040] When the sulfur content in the molten stainless steel is more than 0.015 percent by weight, silver sulfides generated by reactions with the silver increase, and antibacterial properties are degraded because the amount of the silver oxide generated, having superior antibacterial properties, is decreased. Accordingly, in order to obtain superior antibacterial properties, the sulfur content in the molten steel is preferably not more than 0.015 percent by weight.

[0041] According to the present invention, steel raw materials are manufactured from the molten stainless steel having the above-described compositions by continuous casting, preferably under the conditions described above, and if necessary, are subjected to heat treatment at a predetermined temperature followed by hot-rolling, hot-rolled sheets of a given thickness thereby being obtained. The hot-rolled sheets are, if necessary, annealed at 700 to 1,200°C and are applied to desired applications as hot-rolled sheets or cold-rolled sheets having desired thickness processed by the following cold rolling. The cold-rolled sheets are manufactured preferably through annealing at 700 to 1,200°C and, if necessary, through pickling.

Brief Description of the Drawings

[0042]

Fig. 1 is a graph showing the relationship between the reduction rate of number of bacteria and the vanadium content at a surface and a center of a steel sheet.

1. The test piece is sprayed with a 5.0% NaCl aqueous solution (temperature: 35°C) for 0.5 hour, and this is then stored for 1.0 hour at a temperature of 60°C and a humidity not greater than 40%.
2. The test piece is stored for 1.0 hour under the moist conditions at a temperature of 40°C and a humidity not lower than 95%.

[0052] After performing predetermined numbers of cycles for each steel type, ratios of rust areas on the surfaces of the test pieces were measured. The predetermined numbers of cycles were 10 cycles for ferritic stainless steel, 30 cycles for austenitic stainless steel, and 5 cycles for martensitic stainless steel.

[0053] The evaluation results are shown in Tables 3 and 4. In the surface finish level listed in the Tables, 2B and BA are surface finish levels in accordance with JIS G4305, and #320 and #400 are polishing finish levels in accordance with JIS R6001.

[0054] As can be seen from Tables 3 and 4, it was confirmed that steel sheets (Examples of the present invention) containing silver in the range according to the present invention, and a silver oxide in the range according to the present invention, were superior in workability and corrosion resistance. In addition, superior antibacterial properties were confirmed in the evaluation thereof so as to decrease Escherichia coli by not less than 99%, and persistency of antibacterial properties was also superior, decreasing Escherichia coli in a manner similar to the above on test pieces already used for the evaluation of corrosion resistance. The persistency of antibacterial properties was maintained regardless of the surface finish of the steel sheets and sufficient antibacterial properties after polishing could also be confirmed.

[0055] The results described above can be confirmed regardless of the type of the stainless steel, such as ferritic stainless steel, austenitic stainless steel, and martensitic stainless steel.

[0056] In contrast, in the comparative examples, which are outside of the ranges of the present invention, regardless of the type of the stainless steel, reductions in Escherichia coli were small and antibacterial properties were degraded, or the antibacterial properties after the evaluation of corrosion resistance were decreased and the persistency of the antibacterial properties was degraded.

Industrial Applicability

[0057] The present invention provides stainless steel having superior antibacterial properties without degrading corrosion resistance and maintaining the antibacterial properties even after surface finishing, such as polishing, is performed. Therefore, advantages in terms of industrial uses of the stainless steel can therefore be obtained. The stainless steel according to the present invention is suitably used for applications, after forming and polishing are performed, focusing on sanitary aspects in moist environments, such as application in kitchens and baths.

Table 1 (continued)

25	Hafnium	0.01	0.30	0.30	0.03	0.006	13.2	0.009	0.010	-	-	0.04	-	-	-	0.22		0.02	Example of the present invention
26		0.04	0.31	0.30	0.02	0.006	13.0	0.010	0.010	-	-	0.07	-	-	-	1.10		0.01	Comparative example
27		0.31	0.45	0.35	0.03	0.005	13.1	0.025	0.002	-	-	0.25	-	-	-	0.037		0.01	Example of the present invention
28		0.32	0.35	0.45	0.02	0.006	12.6	0.025	0.002	-	-	0.07	-	-	-	0.031		0.02	Example of the present invention
29		0.33	0.34	0.44	0.02	0.006	12.6	0.025	0.002	-	-	0.07	-	-	-	0.031		0.38	Example of the present invention

Table 3

Steel No.	Type	Continuous casting rate m/min	Amount of silver oxide (wt%)	Surface finish level	Corrosion resistance: Ratio of rust area (%)	Antibacterial characteristics: Before corrosion resistance evaluation: Number of living bacteria (cfu/piece)	Before corrosion resistance evaluation: Reduction rate of bacteria (%)	After corrosion resistance evaluation: Number of living bacteria (cfu/piece)	After corrosion resistance evaluation: Reduction rate of bacteria (%)	Remarks
11	Austenite	1.0	0.020	2B	3	<10	>99.9	1.4×10^{4}	99.5	Example of the present
12		1.0	0.019	BA	0	<10	>99.9	<10	>99.9	Example of the present
		1.0	0.019	2B	2	<10	>99.9	<10	>99.9	Example of the present
		1.0	0.019	#320	9	<10	>99.9	<10	>99.9	Example of the present
		0.7	0.0004	2B	17	6.7×10^{4}	97.4	9.2×10^{4}	96.7	Comparative example
		1.8	0.0002	2B	19	2.1×10^{5}	87.5	2.3×10^{5}	87.6	Comparative example
13		1.1	-	2B	5	2.6×10^{5}	0	2.8×10^{5}	0	Comparative example
14		1.2	0.007	2B	2	1.1×10^{3}	>99.9	1.3×10^{3}	>99.9	Example of the present
15		1.5	0.024	2B	3	<10	>99.9	<10	>99.9	Example of the present
16		1.2	0.040	2B	25	<10	>99.9	3.0×10^{5}	89.3	Comparative example
17		1.2	0.040	2B	3	<10	>99.9	2.9×10^{4}	99.0	Example of the present
18		1.2	0.040	2B	19	<10	>99.9	3.0×10^{5}	89.3	Comparative example
21	Martensite	0.9	0.021	#400	5	<10	>99.9	3.9×10^{4}	99.5	Example of the present
22		0.9	0.022	#400	3	<10	>99.9	3.9×10^{4}	99.5	Example of the present
		1.7	0.0001	#400	9	7.0×10^{5}	90.3	7.0×10^{5}	91.4	Comparative example
23		1.0	-	#400	6	7.2×10^{5}	0	8.1×10^{5}	0	Comparative example
24		1.0	0.008	#400	4	2.3×10^{3}	>99.9	1.3×10^{3}	>99.9	Example of the present
25		1.0	0.039	#400	5	<10	>99.9	<10	>99.9	Example of the present
26		1.0	0.041	#400	89	<10	>99.9	8.3×10^{5}	89.8	Comparative example
27		1.1	0.020	#400	17	<10	>99.9	<10	>99.9	Example of the present
28		1.0	0.019	#400	18	<10	>99.9	<10	>99.9	Example of the present
29		1.2	0.016	#400	17	2.5×10^{4}	99.7	3.9×10^{4}	99.5	Example of the present

Claims

1. A stainless steel having antibacterial properties, comprising:

   not less than 10 percent by weight of chromium;
   0.001 to 0.30 percent by weight of silver; and
   not less than 0.0005 percent by weight of a silver oxide, the amount of the silver oxide being not more than 1.1 times the amount of the silver.

2. A stainless steel having antibacterial properties according to Claim 1, further comprising 0.001 to 1.0 percent by weight of vanadium.

3. A stainless steel having antibacterial properties according to one of Claims 1 and 2, further comprising not more than 0.015 percent by weight of sulfur.

4. A stainless steel having antibacterial properties according to any one of Claims 1 to 3, wherein the silver content is 0.001 percent by weight to less than 0.05 percent by weight.

5. A stainless steel having antibacterial properties according to Claim 2, wherein the vanadium content is 0.001 to 0.30 percent by weight.

6. A stainless steel having antibacterial properties according to one of Claims 1 to 5, wherein the stainless steel is in the form of any one of a sheet, a strip, a pipe, and a wire.

7. A method for manufacturing a stainless steel raw material having antibacterial properties, comprising the steps of:

   controlling amounts of not less than 10 percent by weight of chromium, 0.001 to 0.30 percent by weight of silver, and not more than 0.015 percent by weight of sulfur in a molten stainless steel; and
   performing continuous casting of the molten stainless steel at a casting rate of 0.8 to 1.6 m/min.

8. A method for manufacturing a stainless steel having antibacterial properties according to Claim 7, wherein the molten stainless steel further comprising 0.001 to 1.0 percent by weight of vanadium.

9. A method for manufacturing a stainless steel having antibacterial properties according to one of Claims 7 and 8, further comprising steps at hot rolling and cold rolling.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP99/02972

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl' C22C38/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl' C22C38/00-38/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1999
Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT WPI, ANTIMICROBIAL, STAINLESS, STEEL, SILVER, CHROMIUM

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 11-12692, A (Kawasaki Steel Corp.), 19 January, 1999 (19. 01. 99) (Family: none)	1-9
A	JP, 10-259456, A (Nisshin Steel Co., Ltd.), 29 September, 1998 (29. 09. 98) (Family: none)	1-9
A	JP, 11-29879, A (Mitsubishi Materials Corp.), 2 February, 1999 (02. 02. 99) (Family: none)	1-9
A	JP, 9-249948, A (Nisshin Steel Co., Ltd.), 22 September, 1997 (22. 09. 97) (Family: none)	1-9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
7 September, 1999 (07. 09. 99)

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21 September, 1999 (21. 09. 99)

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Japanese Patent Office

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